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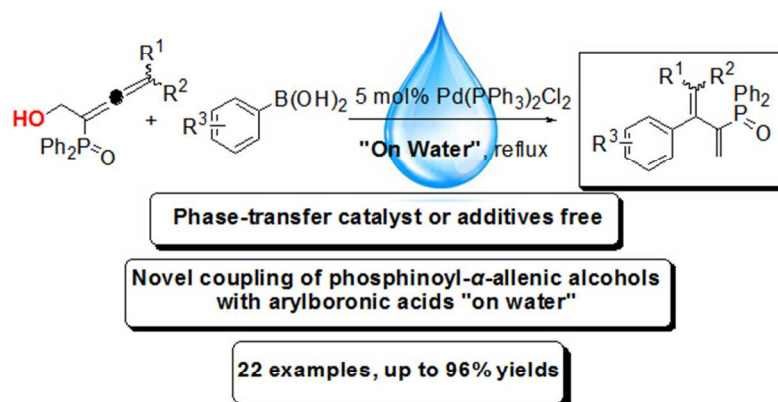
Suzuki-Miyaura Coupling of Phosphinoyl-*α*-Allenic Alcohols with Arylboronic Acids Catalyzed by Palladium Complex "On Water": An Efficient Method to Generate Phosphinoyl 1,3-Butadienes and Derivatives

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We report here the first palladium-catalyzed Suzuki-Miyaura couplings of phosphinoyl-*α*-allenic alcohols with arylboronic acids "on water" without phase-transfer catalysts or additives. This new methodology provides a novel approach to generate phosphinoyl 1,3-butadienes and derivatives with medium to excellent yields. A mechanism *via* initial C(sp^3)-OH bond cleavage of substrate to form *π*-allyl-palladium intermediates, transmetallation with arylboronic acid, followed by reductive elimination to afford product, is proposed.

Introduction

Suzuki-Miyaura cross-coupling[1] catalyzed by transition metals is one of the most versatile approaches for constructing biaryl and alkene derivatives towards key moieties of numerous natural products, agrochemicals, pharmaceuticals, and functional polymers *etc*. Current achievements of the Suzuki-Miyaura coupling have been carried out chiefly by using different ligands and/or metals[1b,2], various reaction media[3]. Noticeable advances have been achieved with conducting reactions in water or aqueous solution. From environmental and economic points of view, water as cheap, readily available, non-toxic and non-flammable solvent has been one of the most important choices for organic transformations in green chemistry. In this respect, a number of remarkable results reported by the groups of Glorius, Beller, Herrman, Nolan, Organ and Köhler *etc.* have been documented conducting the cross-coupling of boronic derivatives with aryl halides in water[2a,4]. In order to improve the catalytic efficiency, efforts are also focused on changing the property

of organoboronic compounds[1a]. However, less attention has been paid on exploring novel substrates except conventional electrophiles including alkyl, aryl, alkenyl and alkynyl groups. Currently, alternative allylic partners[5] possessing electron-deficient bonds, such as acetates, carbonates, halides and pseudohalides, are emerging into hot topic research. Moreover, the allylic/allenic substrates with electron-rich functionality such as C-OR, C-OH are still particularly attractive and challenging[6]. In 2009, Lipshutz *et al.* disclosed the first Suzuki-Miyaura couplings of functionalized allylic ethers with arylboronic acids in water at room temperature with the prescence of phase-transfer catalyst (nonionic amphilic PTS).[6a] Parallel experiments shown the coupling reaction "on water" proceeded sluggishly which further demonstrated the key role of phase-transfer catalyst PTS. On the other hand, the use of allylic alcohols or *α*-allenic alcohols as electrophiles for Suzuki-Miyaura coupling is more attractive with respect to atom-economy, albeit limited examples have been reported in refluxing organic solvents [Scheme 1, a, b][6e,6f,8a-8e]. It is noteworthy that the above processes went through *π*-allyl-palladium intermediates for all of the allylic fragments, no exception to most of the allenic fragments[7]. Interestingly, to the best of our knowledge, the coupling reaction of phosphinoyl-*α*-allenic alcohols with arylboronic acids "on water" has not been reported to date[8] [Scheme 1, c].

Organophosphorus compounds play key roles in catalysis, organic synthesis, biochemistry and materials chemistry, which necessitate their significance in preparation[9]. Phosphinoyl 1,3-dienes as one of the functionalized phosphorous compounds are readily be transformed to other valuable compounds, including allylic phosphonates[10], Diels-Alder cyclization products[11], cyclohexa-dienylphosphonates[12], vinyl allenes[13] and phosphine-functionalized copolymers[14] *etc*. However, to be noted, the conventional methods for synthesizing phosphinoyl 1,3-dienes are problematic and quite limited. Until recently, Han *et al.* reported the first nickel-catalyzed generation of phosphinoyl 1,3-butadienes [Scheme 1, d], consisting of the metal-catalyzed addition of diphenylphosphine oxide and related P(O)H compounds to propargyl alcohols followed by an acid-catalyzed dehydration[15]. Although this method provides quite convenient approach to phosphinoyl 1,3-butadienes, only terminal alkynes can be used, moreover, the adducts suffered from mixtures of *syn*-Markovnikov and *anti*-Markovnikov products. Thus, the potential development with diversity and high selectivity/ efficiency

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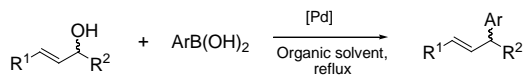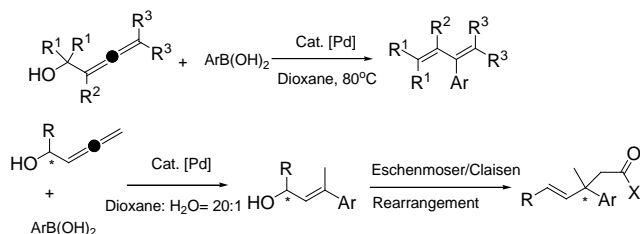*E-mail: rickywu@iccas.ac.cn*
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†Electronic Supplementary Information (ESI) available: [Experinmental procedures and products characterizations]. See DOI: 10.1039/b000000x/
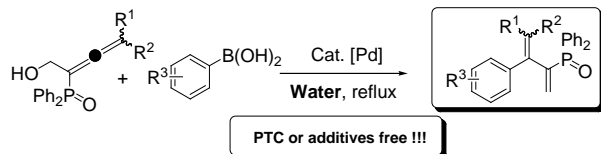
is highly demanded. In continuing research on synthesis and application of organophosphorous chemistry[16], herein we report, for the first time, palladium-catalyzed Suzuki-Miyaura couplings of phosphinoyl-α-allenic alcohols with arylboronic acids "on water" to generate phosphinoyl 1,3-butadienes and derivatives [Scheme 1, c].
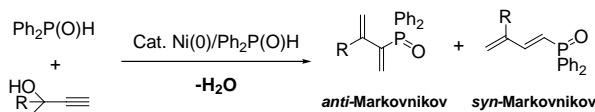

Scheme 1 (a) Palladium catalyzed cross-couplings of allylic alcohols with arylboronic acids; (b) Palladium catalyzed coupling of α-allenic alcohols with arylboronic acids (hydroarylation pathway); (c) This work. (d) Han's first catalytic methods to generate phosphinoyl 1,3-butadienes.

Results and discussions

Initially, a number of metal sources and ligands/additives along with solvents were examined for the cross-coupling of phosphinoyl-α-allenic alcohols (**1a**) with *p*-methoxylphenyl-boronic acid (**2a**) under refluxing temperature (Table 1). Nickel and copper catalysts exhibited no activity to this type of couplings (Entries 1, 2, 6). Rhodium[8f,17], platinum[8b] and palladium sources were proven to be superior to afford medium yields in neat water, thus we extensively screened palladium precursors including $PdCl_2$, $Pd(OAc)_2$, $Pd(TFA)_2$, $(Ph_3P)_4Pd$ and Pd/C. Although phase-transfer catalyst/surfactants were widely used for accelerating Suzuki-Miyaura couplings in water[4l,18], TOABr (Tetraoctylammonium Bromide) and PEG2000 were shown no improvements, instead of furnishing lower yields (Entries 15, 16). Similarly, the presence of organic solvents and bases didn't increase the efficiency. Gratifyingly, the yield was significantly affected by the nature of the ligand and the palladium source. Phosphine ligands were revealed

much higher activities than nitrogen ligands such as 1,10-phenanthroline and 2,2'-bipyridine (Entries 17, 18). To be noted, mono-dentate phosphine ligands underwent smoother transmetallation with arylboronic acids than bidentate phosphine ligands since the latter tended to form coordinatively saturated π-allyl-palladium intermediates towards slower transmetallation, which has been demonstrated by Lipshutz *et al.*[6a]. Eventually, bis(triphenyl-phosphine)palladium chloride was found to be the best catalyst to facilitate the coupling of **1a** and **2a** "on water" under refluxing temperature without phase-transfer catalysts or additives, affording the adduct (**3a**) with 84% yield (Entry 21).

Table 1. Reaction condition optimizations: metal-catalyzed coupling of phosphinoyl-α-allenic alcohol and *p*-methoxyl phenylboronic acid. [a]
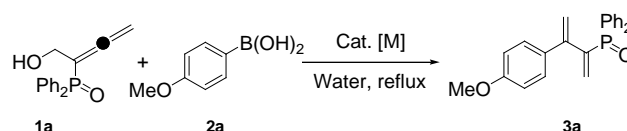
Entry	Catalyst	Solvent /additive/ base	Yield (%)[b]
1	$Ni(OTf)_2$	H_2O	0
2	$Ni(PPh_3)_2Cl_2$	H_2O	0
3	$(PPh_3)_3RhCl$	H_2O	45
4	$Rh_2(OAc)_2$	H_2O	40
5	$PtCl_2$	H_2O	42
6	CuI	H_2O	0
7	$PdCl_2$	H_2O	45
8	Pd/C (10%)	H_2O	0
9	$(Ph_3P)_4Pd$	H_2O	23
10	$Pd(TFA)_2$	H_2O	35
11	$Pd(OAc)_2$	H_2O	46
12	$Pd(OAc)_2$	H_2O/K_2CO_3	46
13	$Pd(OAc)_2$	H_2O/KOH	45
14	$Pd(OAc)_2$	H_2O:Dioxane=9:1/ K_2CO_3	30
15	$Pd(OAc)_2$	$H_2O/TOABr/K_2CO_3$	30
16	$Pd(OAc)_2$	H_2O:PEG2000=3:3.5	29
17	$Pd(OAc)_2$/1,10-Phenanthroline	H_2O	trace
18	$Pd(OAc)_2$ /Bipy	H_2O	trace
19	$Pd(OAc)_2(DPPE)$	H_2O	trace
20	$Pd(TFA)_2(DPPE)$	H_2O	58
21	**$Pd(PPh_3)_2Cl_2$**	**H_2O**	**84**
22	$Pd(PPh_3)_2Cl_2$	H_2O:THF=9:1	59
23	$(BINAP)PdCl_2$	H_2O	56
24	$(Xantphos)PdCl_2$	H_2O	54
25	$Pd(PPh_3)_2Cl_2$	H_2O	0[c]

[a] 1 mmol phosphinoyl-α-allenic alcohol, 2 mmol *p*-methoxyl phenylboronic acid, 10 mL solvent, 5 mol% catalyst, refluxed for 2 hrs; [b] Isolated yield based on allenes; [c] reaction under room temperature for 24hrs.

The optimized conditions from the data in Table 1 (5 mol% $Pd(PPh_3)_2Cl_2$, refluxing water) were generally applicable to several phosphinoyl-α-allenic alcohols and arylboronic acids (Table 2). The coupling of phosphinoyl-α-
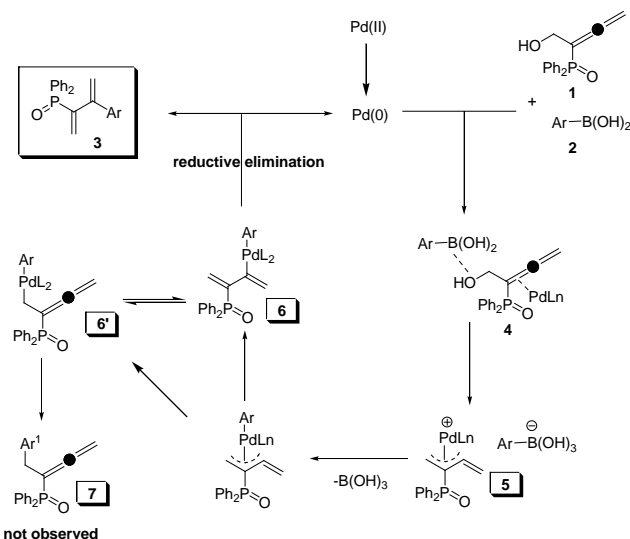
allenic alcohols (**1a**) with arylboronic acids bearing electron-rich or electron-neutral groups were effective to afford phosphinoyl 1,3-butadienes with medium to excellent yields (Entries 1-5). However, arylboronic acids with electron-deficient groups, including -Br, -F and -NO$_2$, led to decrease of coupling yields dramatically even after longer reaction time (Entries, 6-8). This phenomenon might be attributed to the easier polymerization of electron-deficient conjugated dienes especially under heterogeneous high concentration, indicated by the isolation of oligmers. With respect to substituents on phosphinoylallenes, the substrates with groups ranged from alkyl to aromatic, electron-rich to electron-deficient (entries 9-22) were shown medium to excellent yields of phosphinoyl 1,3-butadiene derivatives. For unsymmetrical phosphinolyallenes **1e**, **1h**, the couplings gave exclusively *E*-isomers of **3o**, **3p** and **3u**, respectively. This improved selectivity can be explained by relative differences in the stabilities and reactivities of intermediates affected by the electron-deficient groups on allenes. Notably, substrates with high steric substituents did not impair the catalytic efficiency, remaining yield up to 94% (Entries 19-22). It is worth to mention that all of these substrates afforded comparable yields with terminal phosphinoylallenes (**1a**) even in the case of coupling with electron-deficient arylboronic acids (entries 14, 16, 22).

Table 2. The palladium-catalyzed couplings of substituted phosphinoyl-α-allenic alcohols with various arylboronic acids.[a]

Entry	R^1	R^2	R^3	Yield of **3** [b]
1	H	H(**1a**)	*p*-MeO	84(**3a**)
2	H	H(**1a**)	*p*-Me	82(**3b**)
3	H	H(**1a**)	*o*-Me	96(**3c**)
4	H	H(**1a**)	H	61(**3d**)
5	H	H(**1a**)	Naphthalene	60(**3e**)
6	H	H(**1a**)	*p*-Br	44 (**3f**)
7	H	H(**1a**)	*p*-F	25 (**3g**)
8	H	H(**1a**)	*m*-NO$_2$	25 (**3h**)
9	CH$_3$	CH$_3$ (**1b**)	*p*-MeO	78(**3i**)
10	CH$_3$	CH$_3$ (**1b**)	H	61(**3j**)
11	-C$_5$H$_{10}$- (**1c**)		*o*-Me	90(**3k**)
12	-C$_5$H$_{10}$- (**1c**)		H	73(**3l**)
13	*p*-MeOC$_6$H$_4$	H (**1d**)	H	69(**3m**) [2.9:1] [c]
14	*p*-MeOC$_6$H$_4$	H (**1d**)	*p*-Br	52(**3n**) [7.1:1] [c]
15	*p*-CF$_3$C$_6$H$_4$	CH$_3$ (**1e**)	H	85(**3o**) [only E] [c]
16	*p*-CF$_3$C$_6$H$_4$	CH$_3$ (**1e**)	*p*-F	84(**3p**) [only E] [c]
17	CH$_3$CH$_2$	H (**1f**)	H	73(**3q**) [12:1] [c]
18	CH$_3$CH$_2$	H (**1f**)	*p*-Me	95(**3r**) [12.3:1] [c]
19	Ph	Ph (**1g**)	*p*-MeO	92(**3s**)
20	Ph	Ph (**1g**)	H	94(**3t**)
21	CH$_3$CH$_2$	*p*-ClC$_6$H$_4$(**1h**)	H	72(**3u**) [only E] [c]
22	CH$_3$CH$_2$	*p*-ClC$_6$H$_4$(**1h**)	*m*-NO$_2$	60(**3v**) [2.3:1] [c]

[a] 1 mmol phosphinoyl-α-allenic alcohol, 2 mmol arylboronic acid, 10 mL solvent, reflux; [b] Isolated yield based on allenes; [c] E : Z ratios and relative stereochemistries were determined by ^{31}P-NMR and NOESY experiments, respectively.

Although the mechanism of this reaction is still under exploration, we proposed a catalytic cycle based on the preliminary results and previous studies[6e,6f,19] for the cross-coupling of phosphinoyl-α-allenic alcohol with arylboronic acids "on water" (Scheme 2)[20]. Firstly, the hydroxy group and C=C bond of phosphinoyl-α-allenyl alcohol **1** is activated by arylboronic acids **2** and *in-situ* formed palladium (0) species, respectively. Subsequently, cleavage of allenic carbon-oxygen bond leads to form π-allylpalladium species **5**, which undergoes transmetallation with arylboronic acids to give intermediates **6** and **6'**. No observation of product **7** indicates the priority of forming intermediate **6**. Eventually, reductive elimination of **6** affords the final phosphinoyl 1,3-butadienes **3** and concurrently regenerates palladium (0) species.

Scheme 2. Plausible mechanism for palladium-catalyzed Suzuki-Miyaura coupling of phosphinoyl-α-allenic alcohol with arylboronic acids on water.

Conclusions

In conclusion, we have developed a novel palladium-catalyzed Suzuki-Miyaura coupling of phosphinoyl-α-allenic alcohols with arylboronic acids "on water" without surfactants or additives. In the presence of 5 mol% Pd(PPh$_3$)$_2$Cl$_2$, varieties of phosphinoyl-α-allenic alcohols smoothly coupled with arylboronic acids to afford phosphinoyl 1,3-butadienes and derivatives in medium to excellent yields. This work suggests a new transformation of allenes to phosphinoyl multi-substituted conjugated dienes. Further application of this methodology with tandem reactions to build bioactive compounds is under way.

Experimental

To a 10 mL flask equipped with condenser under nitrogen was added phosphinoyl-α-allenic alcohol (1 mmol), arylboronic acid (2 mmol), Pd(PPh₃)₂Cl₂ (5 mol%), and 10 mL degassed water. The reaction mixture was then heated to reflux for several hours until the complete consuming of starting materials monitored by TLC. After being cooling down, the reaction was extracted with ethyl acetate (5 mL×2). The crude product was purified on flash chromatography, with ethyl acetate/ petroleum ether (1:1) as eluents to afford product.

Acknowledgements

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[ref. 8b] described as below is also conceivable. However, it is difficult to rationalize this mechanism since the aliphatic substitutions on allenes would inevitably lead to by-product **D** via *beta*-hydride elimination, which are not observed. In addition, the hydrolysis of intermediate **B** under current conditions towards by-product allylic alcohol (**C**) should be detected.